Fabrication of Wafer-Scale Uniform Surface Enhanced Raman Scattering (SERS) Substrates for Quantitative Bio Sensing

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We have fabricated highly uniform surface-enhanced Raman scattering (SERS) substrates on 4-inch wafer and used them to conduct precise quantification of analyte molecules. SERS is an attractive technique to analyze materials. The nanoscale features on the substrate amplifies the excitation laser and generate enhanced spectra that show the vibrational energies of the molecules under examination. The most important component in the SERS measurement is a well designed substrate that enhance the excitation light and Raman emission. Various kinds of SERS substrates have already been developed, and some showed extremely high enhancement. However, their fabrication processes are often complex and costly, and the resulting substrates are unsuitable for quantitative measurements. It has been hard to achieve both high uniformity and high enhancement.

The fabrication process consists of sequential wet chemical processes: hydrothermal synthesis of ZnO nanowires (NWs) and liquid phase deposition (LPD) of Au nanoparticles (NPs). A 4-inch Si wafer coated with a ZnO-seed layer was immersed in ZnO-NW precursor solution and heated to 95 °C. Then, the wafer was immersed to Au-NP precursor solution, heated to 90 °C, and rocked back and forth to continuously mix the solution. This LPD process was repeated 5 times to guarantee sufficient coverage of Au NPs.

When inspected with bare eyes, the substrate looked uniformly black. In SEM images, we observed clusters of 10-20-nm diameter Au NPs efficient stacked using the ZnO NWs as frames. In order to evaluate its SERS performance and spatial uniformity, the substrate was incubated in 1 mM benzenethiol (BT) solution and scanned using 785-nm laser at a step of 500 µm. The SERS spectrum showed clear peak of BT at 999, 1022, 1072 cm⁻¹. The SERS intensities of those peaks were uniform throughout the entire substrate, with ±10 % standard deviation.

To demonstrate quantitative measurements, we incubated the substrate in varying concentrations (10 nM - 10 µM) of adenine solution. We tracked the large SERS peak of adenine at 735 cm⁻¹ and obtained the relationship between concentration and intensity as $I = 2.45 \times 10^6 C^{0.4302} - 73.38$, where $I$ and $C$ are SERS intensity and molar concentration of the solution, respectively. In order to verify accuracy of our approach, we prepared 60 nM, 200 nM and 4 µM adenine solution separately and applied to the SERS substrate. Our method produced the concentration of 63.1 nM, 213.3 nM and 3.71 µM, respectively, matching well with the given concentration with 10% accuracy.

We have fabricated wafer-scale SERS substrates by simple wet chemical processes and verified its high sensitivity and uniformity experimentally. Our substrate can be potentially and widely utilized as commercial SERS substrates for quantitative biological and chemical sensing applications.